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DESIGN OF AN ACIDIC NATURAL GAS PURIFICATION PLANT BY MEANS OF A PROCESS SIMULATOR

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One of the most used techniques for gas purification from CO_2 and H_2S is chemical absorption by means of an amine solution. This technique is energy-demanding and requires an accurate design of the removal-regeneration system which usually consists of an absorber followed by a stripping unit.
Processes for the combined removal of CO_2 and H_2S have two main fields of application: natural gas (NG) plants and refinery gas purification units.
This paper is mainly focused on the typical approach of an engineering company when dealing with the design of a purification unit using commercially available process simulators. The case study described in this paper refers to a large size NG plant located in the Emirates.
Emphasis is given to the way an engineering company approaches the design task with the constraint of the different types of guarantees that a customer may require.

1. INTRODUCTION

Acidic gas treatment processes have two main practical industrial application fields: NG purification plants and refinery gas purification units. NG purification plants are typically characterized by very high gas flow rates and relatively low H_2S and CO_2 concentration, as well as high pressures. The guaranteed values are stringent, because the purified gas is the final product of the plant, and the large quantities of gas to be treated heavily affect on the operating costs, namely on the overall utilities consumptions. In the case of refinery gas purification, on the other hand, the flow rates are lower but with higher H_2S concentration. However, the H_2S and CO_2 concentration requirements in the clean gas are less stringent, because the purified gas will not be introduced into the distribution pipe network.
Acidic gas removal processes have been widely used for many decades in the industrial field and many licensed processes are available, the license mainly consisting of patents related to proprietary amines.
Due to this widespread utilization, there are also many plants that use "open art" processes with traditional amines. It is therefore not infrequent that an EPC (Engineering, Procurement, and Construction) contractor can be involved directly in the plant process design without having a third-party licensing company that provides all process information and relevant performance guarantees.

2. PERFORMANCE GUARANTEES IN EPC CONTRACTS

Typical contractual schemes used in gas plants project are reimbursable (cost plus) and lump sum (in particular lump sum turnkey).The second one is widely used in international bids and in this case the responsibility and risk is over the contractor, that must guarantee among all, the performances of the plant.
But what happens if during the test runs the performances are not reached?
If the difference between the actual value and the guaranteed value is below or equal to a certain gap (or percentage) indicated in the contract, the underperformance can be compensated with the formula of

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LIQUIDATED DAMAGES, if the difference between the actual value and the guaranteed value is over such limit, many contracts foresee the MAKE GOOD as remedial action.
In case of LIQUIDATED DAMAGES, the liable contractor will indemnify the loss of performance by paying a penalty proportional to the difference between the guaranteed and the actual values for a specified parameter.
In case of MAKE GOOD, the liable contractor must modify and adjust the plant in order to reach the minimum performance value specified in the Contract.
In case of an "OPEN ART" process the performance guarantee risks cannot be back charged on a technology licensor, and the same must be evaluated and considered in the project contingencies by the EPC contractor that often doesn't have the sensitivity necessary to evaluate the requested data.
It is necessary to increase the knowledge of the problem so to have a better estimation of the possible unknown costs and to reduce the contingencies allocated for the risks of the project.
For example, on a large sweetening unit with an absorber column having a typical diameter of about 5 - 6 meters, height of about 50 meter as well as a stripper column having the diameter of about 6-7 meters and height of about 40 meter, the capital expenditure and the risk magnitude could be really huge, evaluated several millions of euro. Due to it, also small changes into the size of these equipment and the other auxiliary items connected to them can give a significant cost saving or cost increase.
Some of the problems that must be solved by the EPC contractor's process engineers, when the sizing of purification unit falls into its scope of work, are the following:
1) the impact of some hydrocarbon by-products like COS, aromatics, mercaptans, that could potentially modify the absorption behavior of the amine solution in comparison with H_2S and CO_2. This behavior is not as well known as expected but some parameters are requested by the Client as a guaranteed value (in terms of total organic sulfur into the clean gas): for instance BTX (Benzene, Toluene, Xylenes) concentration on acidic gas.
2) H_2S and CO_2 specification on the clean gas must be fulfilled but it is at the same time important not to exceed also the quantity absorbed into the amine solution in case the rich gas is then sent to a SRU (Sulphur Recovery Unit) because it could exceed the design values of that plant, not always under the control of the same engineering company; moreover if the CO_2 absorption is more than what requested by the guarantees, it may represent a production loss in terms of the amount of clean gas sent to the network.
3) since the Clients want to minimize the operating costs of the plant, in general they tend to impose some other constraints like, for instance, the maximum steam consumption of the rich amine regeneration reboiler and the solvent circulation flow rate. This way, the safety margins available to cover the uncertainties of the system (namely process units over sizing) are drastically reduced and the risks for the engineering company are consequently increased.
The typical approach to this problem is to simulate the plant using commercial process simulator software, if possible with two different tools, so to check if the required specification values can be achieved and which are the changes to be applied when it is requested to endorse a preliminary project (FEED) prepared and received from another company.
As highlighted, it is very important that such tools give "each other consistent" and reliable results but unfortunately this is not what happens in practice: most of the times the results of the simulations are not in line each other and, depending on the software used for the simulation, it is possible to have results that are close to the guaranteed values. Being not completely confident in the simulation results, it is not possible for the EPC contractor to know whether the size of the equipment specified in the FEED will allow the fulfillment of the performance guarantees.
In order to cover all the possible process design risks, it is really important to know well where and what are the limits and the reliability of these tools.

3. MODELING OF CHEMICAL ABSORPTION PROCESS

Thermodynamics, kinetics and mass transfer influence the chemical absorption process. Vapor-liquid equilibrium (VLE) modeling must be properly approached (Gamba et al., 2009; Pellegrini et al., 2010; Pellegrini et al, 2011a; Pellegrini et al, 2011b; Pellegrini et al, 2011c): acidic gases and amines are weak electrolytes, which partially dissociate in the aqueous phase. For the VLE description of these systems, commercial process simulators (ASPEN HYSYS®, 2009; ASPEN Plus®, 2009; ProMax®, 2009) employ a γ/ϕ method.
Kinetics and mass transfer can be described using two different approaches: the "equilibrium-based stage efficiency" model or the "rate-based" one. The "equilibrium-based stage efficiency" approach corrects the performance of a theoretical stage by a factor called "stage efficiency". It takes into account mass transfer and non equilibrium chemical reactions for all species (ASPEN HYSYS®) or only mass transfer for non reactive species, when kinetics is considered (ProMax®).
The "rate-based" model analyses the mass and heat transfer phenomena that occur on a real tray or actual packing height, avoiding the approximation of efficiency. In ASPEN Plus® the prediction of mass transfer coefficients is based on the film theory by Lewis and Whitman (1924) and proper kinetic expressions are implemented.

4. SIMULATION OF NATURAL GAS PURIFICATION UNITS

4.1 First case study: a plant under construction

The steady increase in the use of natural gas (Zucca et al., 2005; Pellegrini et al., 2005) makes necessary an up to date analysis and optimization of the consolidated processes for gas purification especially for what concerns the removal of acid gases. The case studied in this work regards a gas sweetening unit with MDEA in a large size NG plant (Pellegrini et al., 2011c), reported in Fig. 1.
It consists of an absorption section followed by a regeneration one. The sour gas stream entering the system has a temperature of 310.15 K, a pressure of 61.5 bar, and a flow rate of about 32000 kmol/h; its composition is reported in Table 1.
The purification is obtained using an aqueous solution of MDEA (45% w/w), whose acidic gases loading should not exceed 0.45 mol/mol, according to customer requirements.
The absorption section consists of two columns (Table 2). The first column performs a bulk acid gas removal, while the second one (that is smaller) has the aim of further reducing the amount of both H_2S and CO_2 to low levels.
The rich solvent is preheated to 380.15 K and fed to the regeneration column where CO_2 and H_2S are removed from the amine solution. The obtained gas, rich in hydrogen sulphide, is fed to a SRU.

Table 1: Composition of the gaseous stream entering the purification system (sour gas)

compound	%mol	compound	%mol
H_2S	4.3313	n-Hexane	0.2414
CO_2	5.1515	n-Heptane	0.0681
H_2O	0.1	n-Octane	0.013
Nitrogen	0.2301	n-Nonane	0.0019
Methane	70.6804	n-Decane	0.0002
Ethane	9.3927	Benzene	0.0193
Propane	5.6016	Toluene	0.0095
i-Butane	1.0203	Methyl Mercaptan	0.0048
n-Butane	2.0706	Ethyl Mercaptan	0.0085
i-Pentane	0.5101	COS	0.0045
n-Pentane	0.5402		

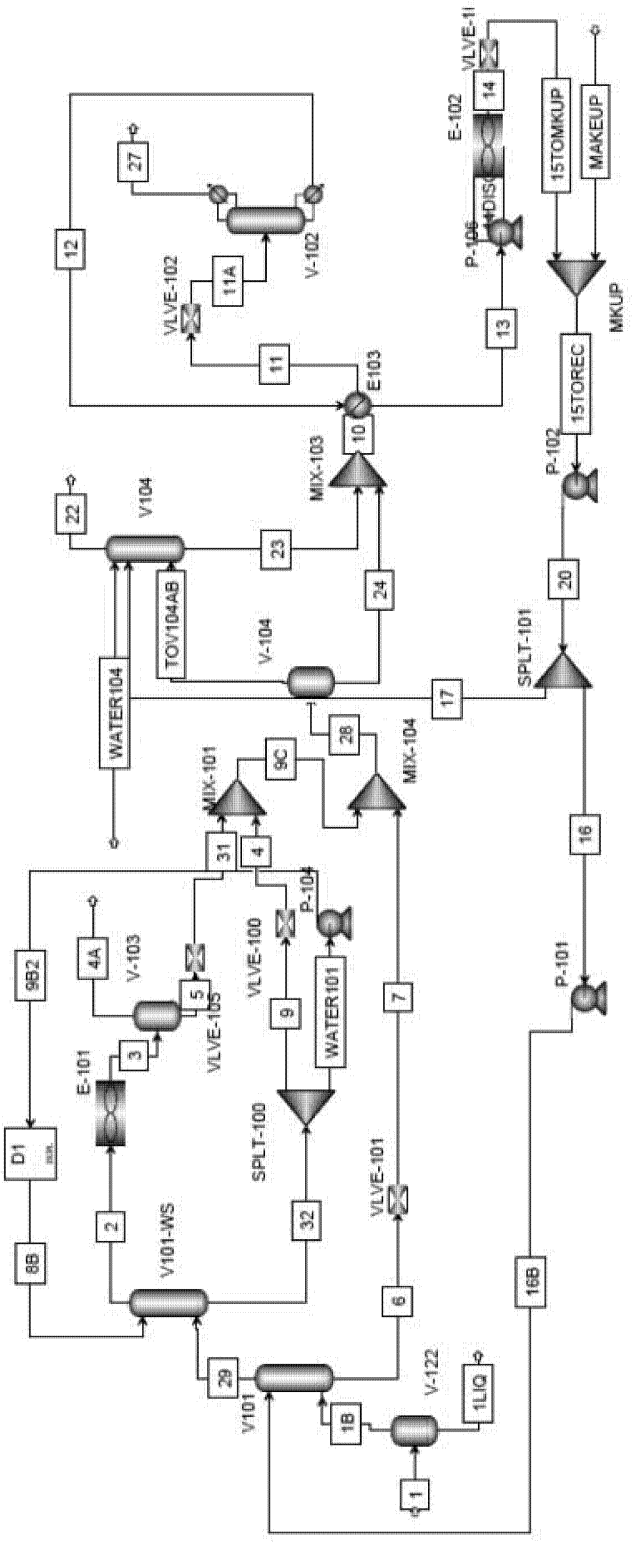

Fig. 1: Scheme of the simulated plant (as from ASPEN Plus®).

Table 2: Characteristics of the two columns in the absorption section

Parameter	high pressure column	low pressure column
diameter [m]	6.2	0.9
type of column	tray column	packing column
packing / tray type	Nutter float valve	Pall ring 1in
packing height [m]/number of trays	32	9
pressure [bar]	60.4	9.48

4.2 **Second case study: a plant from literature**

Simulations of a plant whose experimental data are available are needed in order to verify the agreement between calculated and experimental plant performances.

Experimental data of a few operating plants are available in literature. In particular, Dome's North Carolina Plant has been analyzed (Daviet et al., 1984). The plant was designed and built for natural gas sweetening. The aim is to remove H_2S and CO_2 in order to attain pipeline specifications (2% CO_2 and ¼ grains H_2S/100 SCF (Daviet et al., 1984)).

The plant is shown in Fig. 2.

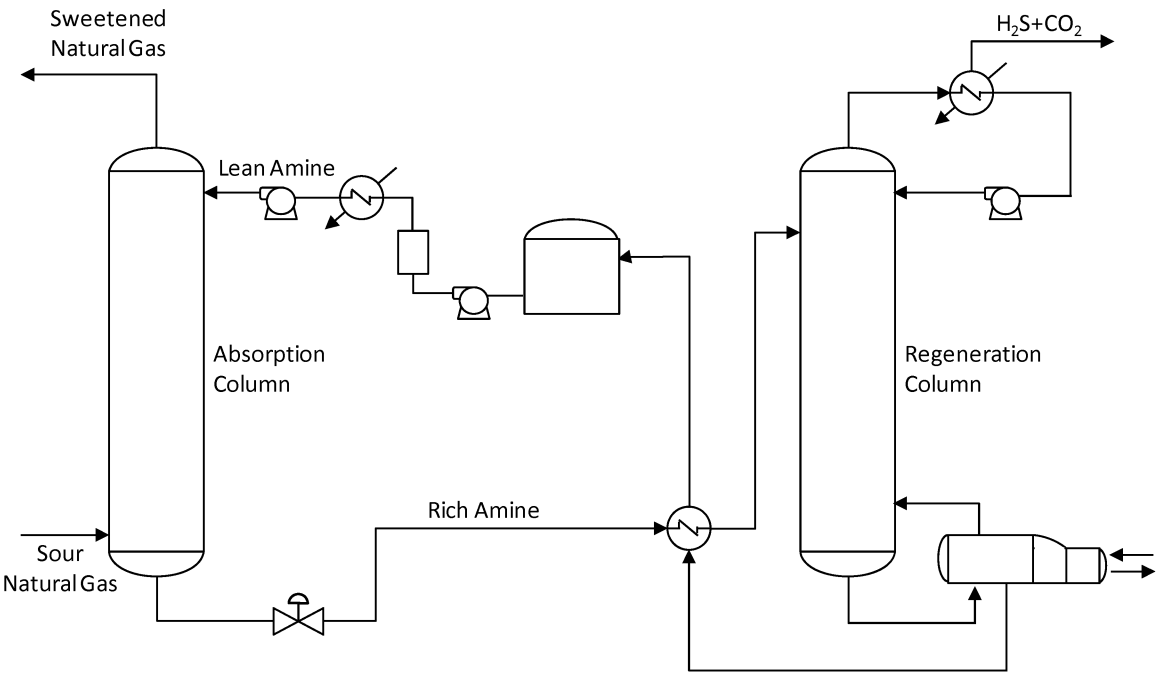

Fig. 2: Scheme of the Dome's North Carolina Plant.

It is composed of one absorber and one stripper. The gas fed to the absorption column is contacted with a 33% MDEA aqueous solution.
Since in Daviet et al. (1984) data for the absorber alone are reported, the regeneration column was not simulated. The absorber behaviour was studied as a function of the amine flow rate to the absorption column (Daviet et al., 1984). For this reason, five case studies are reported: conditions of the inlet gas are almost the same, whereas the amine flow rate drastically changes.
For each case, the inlet conditions to the absorber (GASIN and LEANIN) are shown in Table 3 and in Table 4.
The absorption column has a diameter of 1.28 m and contains 21 valve trays.
The operating pressure is 55 bar.

Table 3: Characteristics of the sour natural gas fed to the absorber in Dome's North Carolina Plant

compound	case 1	case 2	case 3	case 4	case 5
T [K]	302.0	302.6	305.4	306.5	306.5
P [bar]	55.16	55.16	55.16	55.16	55.16
flow rate [kmol/h]	1541.94	1553.90	1642.64	1470.23	1506.09
mole fraction					
H_2S	0.000050	0.000058	0.000056	0.000058	0.000055
CO_2	0.035200	0.034700	0.034693	0.034700	0.034800
H_2O	0.000874	0.000874	0.000874	0.000874	0.000874
Methane	0.963876	0.964368	0.964376	0.964368	0.964271

Table 4: Characteristics of the lean amine solution fed to the absorber in Dome's North Carolina Plant

compound	case 1	case 2	case 3	case 4	case 5
T [K]	309.3	310.9	317	319.3	322
P [bar]	55	55	55	55	55
flow rate [kmol/h]	644.28	772.32	921.66	1068.36	1129.84
mole fraction					
H_2S	0.000200	0.000161	0.000290	0.000250	-0.000169
CO_2	0.000452	0.000488	0.000405	0.000406	0.000522
H_2O	0.930000	0.930000	0.930000	0.930000	0.930000
Methane	0	0	0	0	0
MDEA	0.069348	0.069351	0.069305	0.069344	0.069647

5. RESULTS AND DISCUSSION

The two plants have been simulated by means of different commercial software. In both cases, results from process simulators are not in agreement.
Simulation results for the plant under construction are shown in Fig. 3.
Removal of carbon dioxide with ASPEN Plus® is higher than with the other process simulators (Fig. 3a)): the first column removes most of the CO_2 from the natural gas stream, with no selectivity toward H_2S. The upper part of the column is not effective: design with ASPEN Plus® requires a lower number of trays compared with the other simulators.
Differences in acidic gas removal correspond to differences in temperature profile (Fig. 3b)). The bulge is located at the bottom of the column, as usual for this system (Kohl and Nielsen, 1997), but the value of the maximum temperature in the absorber varies of about 15°C, leading to different temperatures at the bottom of the column and of the liquid outlet stream.
Results of the simulation of the case from literature (Daviet et al., 1984) are shown in Fig. 4 and in Fig. 5.

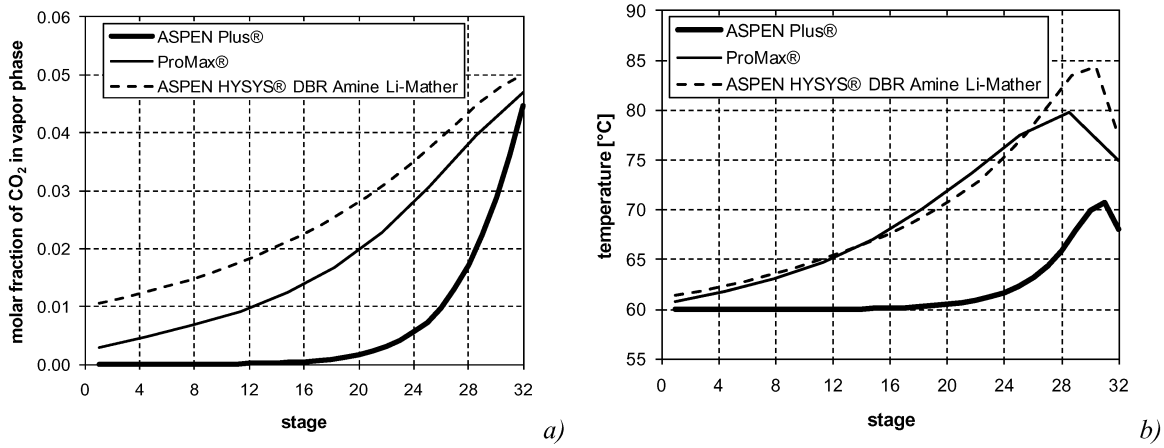

Fig. 3: a) Molar fraction profile of CO_2 in vapour phase and b) temperature profile along the high pressure absorption column obtained with different process simulators.

Outputs obtained by TSWEET® as reported in Daviet et al. (1984) have been added to our results. The program performs calculation using a modified Kent and Eisenberg (1976) equilibrium model for vapour pressures. TSWEET® rate of carbon dioxide absorption is obtained through the use of a kinetic model similar to the one implemented in ProMax® (Pellegrini et al., 2011c).
By comparison among the different simulators, also in this case ASPEN Plus® shows a higher absorption of both H_2S and CO_2.
On the contrary, ProMax® seems to be the most conservative, calculating a carbon dioxide and hydrogen sulphide content in the gas leaving the absorber higher than experimental data. A similar behaviour can be seen in Fig. 4 and in Fig. 5 for TSWEET®, which is based on the same kinetic approach.

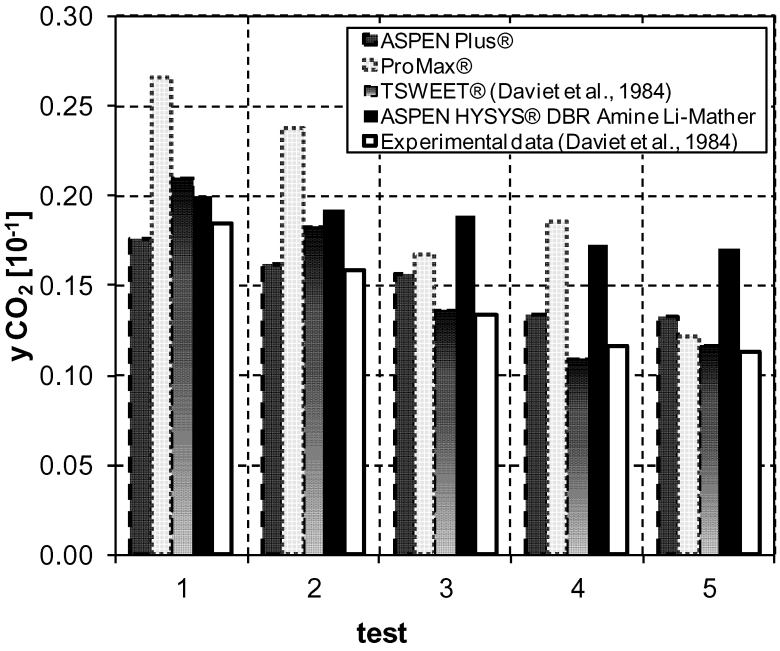

Fig. 4: Molar fraction of CO_2 in the sweetened gas coming from the absorption column obtained with different process simulators.

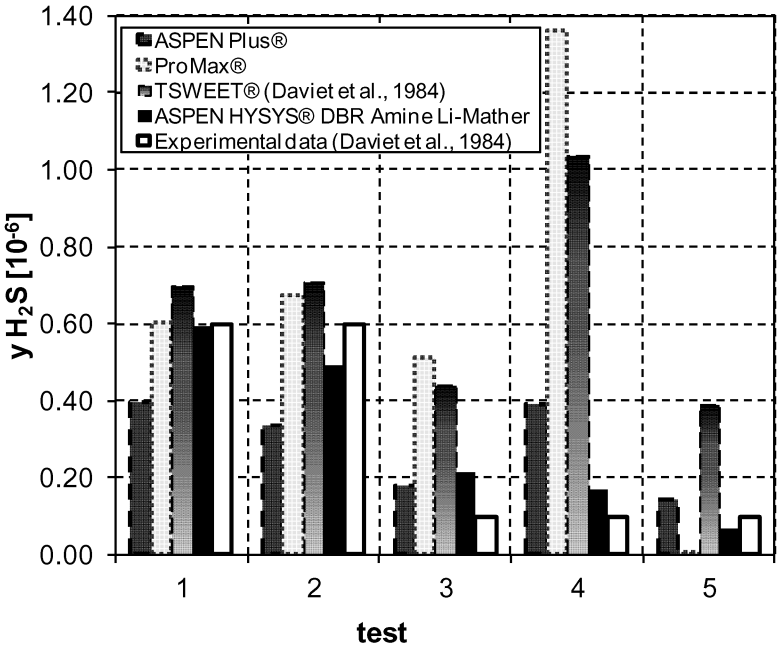

Fig. 5: Molar fraction of H_2S in the sweetened gas coming from the absorption column obtained with different process simulators.

For a better comparison temperature profiles along the absorber from experimental data and different simulation packages are reported in Fig. 6.

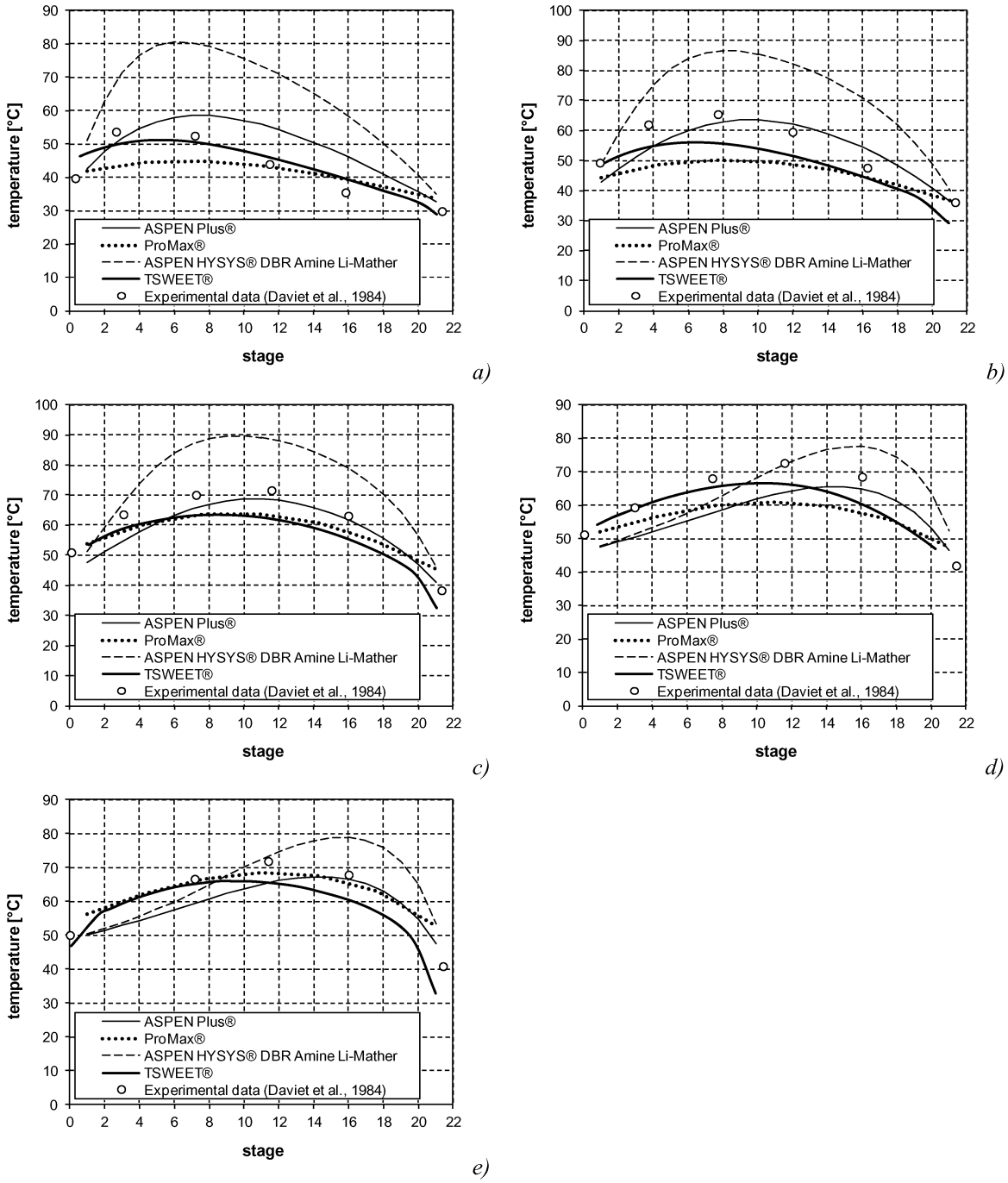

Fig. 6: Temperature profile along the high pressure absorption column obtained with different process simulators: a) test 1, b) test 2, c) test 3, d) test 4 and e) test 5 of the Dome's North Carolina Plant.

The differences obtained in the simulation results suggest that the calculation approach ("rate-based" or "equilibrium-based stage efficiency") as well as the thermodynamic, kinetic and mass transfer correlations must be carefully checked and chosen.

6. CONCLUSIONS

In order to reduce uncertainties in plant design and to be sure to fulfill the more and more stringent contractual guarantees, it is a common and advisable practice of engineering companies to compare simulation results from different process simulators. Taking as case study a large NG plant under construction in the Emirates and experimental data of the Dome's North Carolina Plant (Daviet et al., 1984), the reliability of simulation results has been checked using a "rate-based" model as well as "equilibrium-based stage efficiency" approaches. The obtained results show significant differences, suggesting that a deeper insight of the theories on which the models are based and of the way such models are implemented in the simulators is advisable.

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